Key Terms

reaction rate
average rate of reaction
instantaneous rate of reaction
collision theory
activation energy, E_a
activated complex
catalyst
enzyme
initial rate
reaction mechanism
elementary step
intermediate
rate-determining step

Chemical Reaction Rates (6.1)

Closely connected to thermodynamics is chemical kinetics, the field of chemistry that investigates the rate at which reactions occur. A rate describes a change in a quantity over a given time interval. Rate can be expressed as the following general mathematical equation:

$$\text{rate} = \frac{\Delta\text{quantity}}{\Delta t}$$

For a chemical reaction, the **reaction rate** is the change in the amount of reactants or products present over a given time interval. A reaction rate is usually expressed as the change in concentration of a reactant or product per unit time. For example, the following equation expresses rate as a function of the rate of change of the concentration of reactant A over time.

$$\text{reaction rate} = \frac{[\text{A}]_{\text{final}} - [\text{A}]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

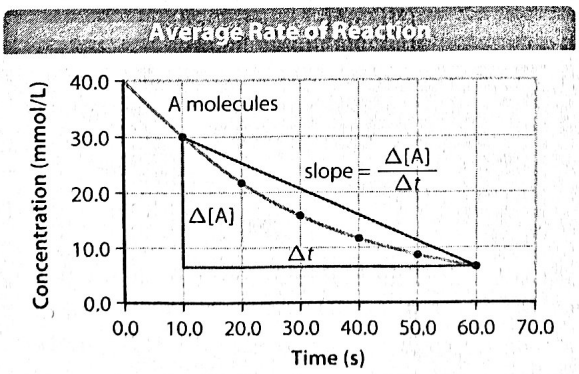
$$= \frac{\Delta[\text{A}]}{\Delta t}$$

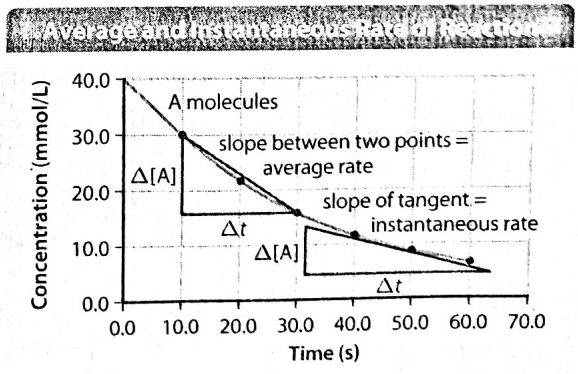
Because reactants are used up in chemical reactions, their concentration decreases over time and the value of $\Delta[\text{A}]$ is negative. To express the reaction rate as a positive number, $\Delta[\text{A}]$ is therefore multiplied by -1.

Determining Reaction Rates (6.1)

Rates of reaction must be determined by experiment. Chemists determine a rate of reaction by measuring the *decrease* in concentration of a reactant or the *increase* in concentration of a product. A rate of reaction calculated for any time interval is an **average rate of reaction**. An average rate of reaction is equal to the slope of the line that connects the two points that define the time interval, as shown in the graph on the left.

A rate of reaction at any particular time is an **instantaneous rate of reaction**. Such a rate is equal to the slope of a line tangent to the concentration vs. time curve at that point in time. The graph on the right compares average rate of reaction with instantaneous rate of reaction.

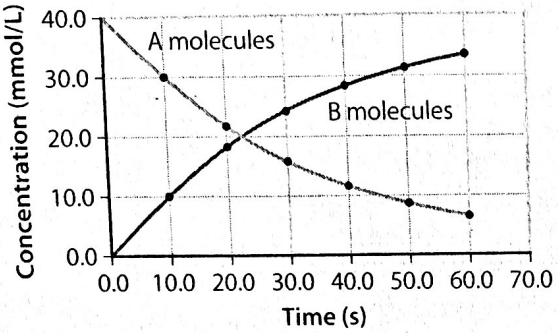




ning Check

The graph below shows concentrations of a reactant and a product during the course of a chemical reaction. Use the graph to answer the following questions.

Progress of Reaction



1. K/U Are the A molecules the reactant or product in the reaction?

_____

_____

2. K/U Are the B molecules the reactant or product in the reaction?

_____

_____

3. K/U Describe the changing slope of the line for the B molecules, and explain what it means.

_____

_____

4. T/I What information about the reaction can be determined from the point at which the lines on the graph intersect?

_____

_____

Study Tip

When analyzing a graph, talk through what is happening along the timeline to be sure you understand what the graph is communicating. For example, "At first there is a high concentration of A molecules and there are zero molecules. The concentration of A molecules decrease as the concentration of B molecules increase."

Expressing Reaction Rates (6.1)

Using experimental data about a reactant or product, you can calculate and express an average reaction rate in terms of the concentration of that substance, as shown in the first sample problem on the next page. You can use the coefficients of the balanced chemical equation of a reaction to determine the relationship between rates of reaction in terms of different substances in the reaction, as shown in second sample problem. By measuring the rate of change in the concentration of just one reactant or product, you can calculate the rate of change of the concentration of all the other substances in the reaction based on the mole ratios for the reactants and products.

Sample Problem: Calculating an Average Reaction Rate

Problem

In a decomposition reaction represented by $2AB \rightarrow A_2 + B_2$, the concentration of product B_2 after 3.60 min is 7.50×10^{-1} mol/L and after 4.80 min 8.70×10^{-1} mol/L. Calculate the average reaction rate, per second, in terms of B_2, between 3.60 min and 4.80 min.

What Is Required?

You need to calculate the average rate at which product B_2 is formed in the period from 3.60 min to 4.80 min.

What Is Given?

You know the initial time: $t_{initial} = 3.60$ min
You know the final time: $t_{final} = 4.80$ min
You know the initial concentration of the product: $[B_2]_{initial} = 7.50 \times 10^{-1}$ mol/L
You know the final concentration of the product: $[B_2]_{final} = 8.70 \times 10^{-1}$ mol/L

Plan Your Strategy	Act on Your Strategy
Convert the initial and final times from minutes to seconds.	$t_{initial} = 3.60 \text{ min}$ $= 3.60 \cancel{\text{min}} \times 60 \frac{\text{s}}{\cancel{\text{min}}}$ $= 216 \text{ s}$ $t_{final} = 4.80 \text{ min}$ $= 4.80 \cancel{\text{min}} \times 60 \frac{\text{s}}{\cancel{\text{min}}}$ $= 288 \text{ s}$
Write the equation for the average rate of increase of product.	$\text{average rate} = \frac{\Delta[B_2]}{\Delta t}$ $= \frac{[B_2]_{final} - [B_2]_{initial}}{t_{final} - t_{final}}$
Substitute the numerical values into the equation. Then solve the equation.	$\text{average rate} = \frac{[A]_{final} - [B_2]_{initial}}{t_{final} - t_{final}}$ $= \frac{\_\_\_\_\_ - \_\_\_\_\_}{\_\_\_\_\_ - \_\_\_\_\_}$ $= \_\_\_\_\_$ $= \_\_\_\_\_$ The average rate at which B_2 is formed during the time period is _____ mol/L·s.

Check Your Solution

Check that the average reaction rate is reasonable given the initial and final concentrations of B_2. Check that the answer is correctly expressed in two significant digits. Check that the answer is expressed in units of mol/L·s.

Sample Problem: Determining Reaction Rates in Terms of Products and Reactants

Problem

Gaseous ammonia, $NH_3(g)$, reacts with oxygen to form nitrous oxide, NO(g), and water vapour, according to the following equation:

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightarrow 2NO(g) + 3H_2O(g)$$

NO(g) is produced at a rate of 0.060 mol/L·s.

a. What is the rate of decomposition of $NH_3(g)$?

b. What is the corresponding rate of formation of $H_2O(g)$?

What Is Required?

Because $NH_3(g)$ is a reactant, you need to calculate its rate of decomposition.
$H_2O(g)$ is a product, so you need to determine its rate of formation.

What Is Given?

You know the rate of formation of nitrous oxide: rate $= \frac{\Delta[NO]}{\Delta t} = 0.060$ mol/L·s
You know the balanced chemical equation for the reaction:

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightarrow 2NO(g) + 3H_2O(g)$$

Plan Your Strategy	Act on Your Strategy
a. Determine the ratio of $NH_3(g)$ to NO(g).	2 mol of NH_3 is decomposed for every 2 mol of NO formed, or $\frac{NH_3}{NO} = \frac{2}{2} = \frac{1}{1}$
Use the coefficients in the balanced chemical equation to determine the relative rate of decomposition of $NH_3(g)$.	For every mole of NO that is formed, 1 mol of NH_3 is decomposed.
Write the equation for the rate of decomposition of $NH_3(g)$ relative to the formation of NO. Substitute the numerical values into the equation and solve.	$\frac{\Delta[NH_3]}{\Delta t} = \frac{1}{1}\left(\frac{\Delta[NO]}{\Delta t}\right)$ The rate of consumption of $NH_3(g)$ is 0.060 mol/L·s.
b. Determine the ratio of $H_2O(g)$ to NO(g).	____ mol of H_2O is formed for every _____ mol of NO formed, or $\frac{H_2O}{NO} =$ _____ For every mole of NO formed, _____ mol of H_2O is formed.
Use the coefficients in the balanced equation to determine the relative rate of formation of $H_2O(g)$. Write the equation for the rate of formation of $H_2O(g)$ relative to the rate of formation of NO(g). Substitute the numerical values into the equation and solve.	$\frac{\Delta[H_2O]}{\Delta t} =$ _____ $\left(\frac{\Delta[NO]}{\Delta t}\right)$ = _____ × _____ = _____ The rate of formation of $H_2O(g)$ is _____ mol/L·s.

Check Your Solution

Check that there are two significant digits in the answer. Check that your answer makes sense. The rate of formation of water should be greater than the rate of formation of nitrogen monoxide.

Measuring Rates of Reaction Experimentally (6.1)

Chemists use measurable properties of the substances in a reaction to determine reaction rates. These properties and the equipment typically used to measure them include

- the volume of gas formed, measured with a gas syringe
- the change in mass of reactants or products, measured with a balance
- the change in pressure in a closed container for a gas-phase reaction, measured with a pressure sensor
- a change in colour, measured with a spectrophotometer
- a change in pH, measured with a pH meter
- a change in electrical conductivity, measured with a conductivity probe

Measurement involves monitoring the change in a property to determine the rate at which a reactant is consumed or a product is formed.

Study Tip

When considering how a reaction rate can be measured, pay close attention to the states of matter of the substances involved, as well as their other properties. Is an acid involved? Is a gas produced? Does an electrolytic solution form? Is there a colour change?

Learning Check

1. T/I Consider the following reaction:

$$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

Under certain conditions, the concentration of $N_2O(g)$ is 0.034 mol/L at 32 s, and 0.058 mol/L at 281 s. What is the average reaction rate over this time period in terms of production of $N_2O(g)$?

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2. T/I Under a certain set of conditions, the rate of production of $NO_2(g)$ in the following reaction is 0.643 mol/L·s. What is the corresponding rate of consumption of NO(g)?

$$NO(g) + NO_3(g) \rightarrow 2NO_2(g)$$

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3. T/I Consider the following chemical reaction:

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(\ell)$$

All of the dissolved substances involved in this reaction are colourless, except $Cu(NO_3)_2(aq)$ which gives the solution a blue colour.

a. What change in colour would you expect to observe in the solution as the reaction progressed?

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b. What instrument could you use to measure the rate of the reaction?

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4. Consider the following chemical reaction.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Suggest two different ways you could measure the rate of reaction.
